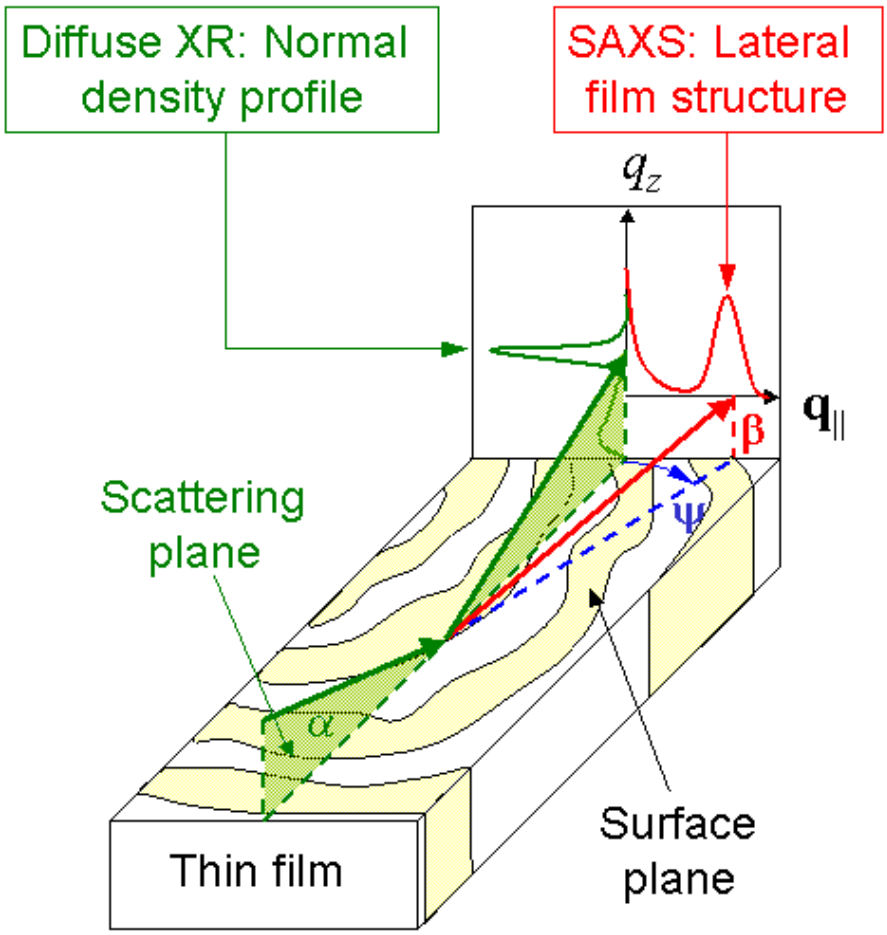
GISAXS: A Versatile Tool for the Study of Structure and Kinetics of Organic Thin Films on Nanoscopic Length Scales

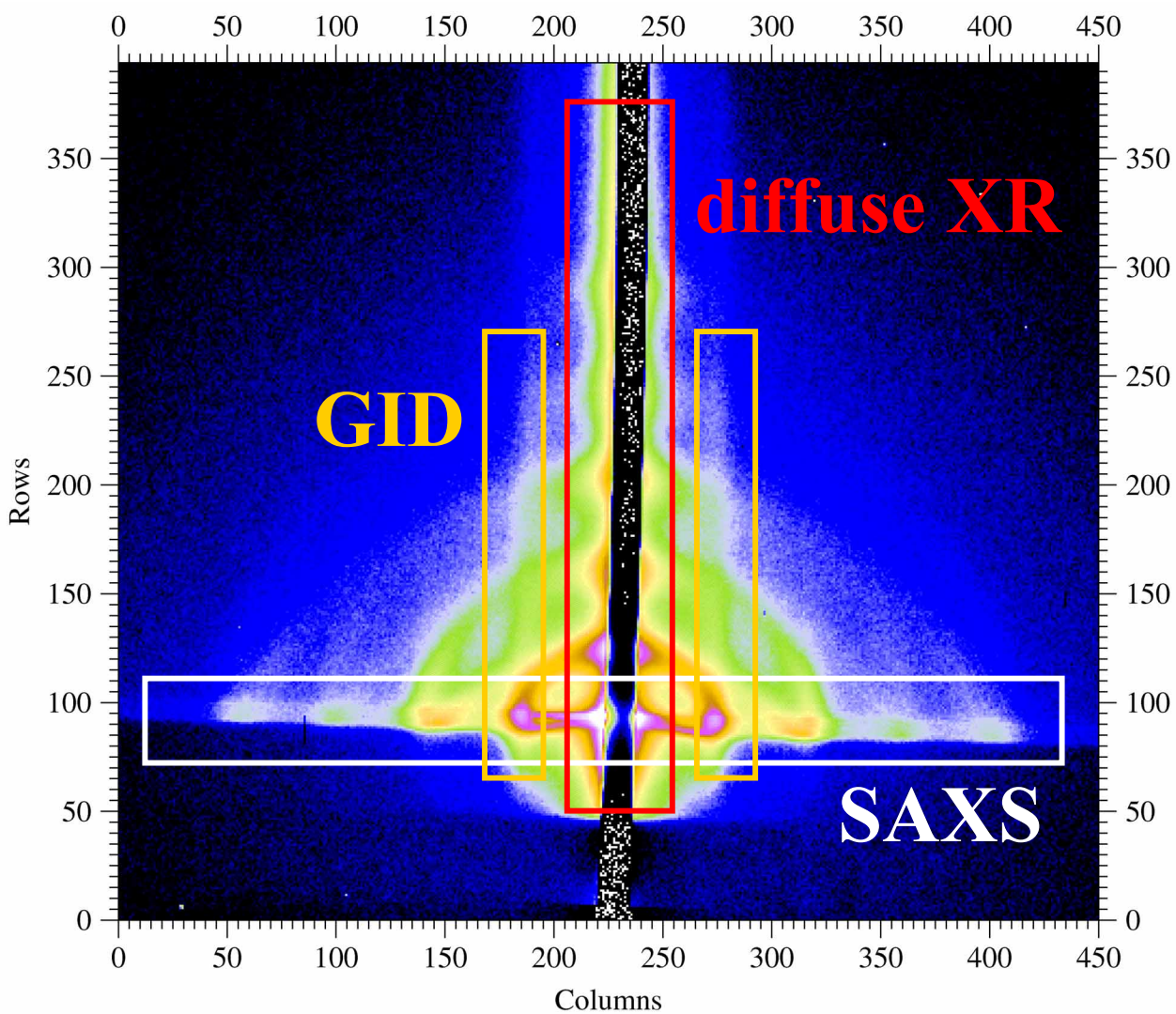
Detlef-M. Smilgies
CHESS G-line Division
Cornell University

Small-angle Scattering Under Grazing-incidence (GISAXS)



Period	Scattering Angle @ 10 keV
10 nm	0.7º
100 nm	0.07º

Scattering Contributions – Scattering Communities



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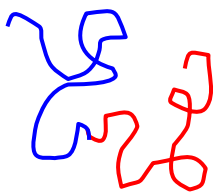
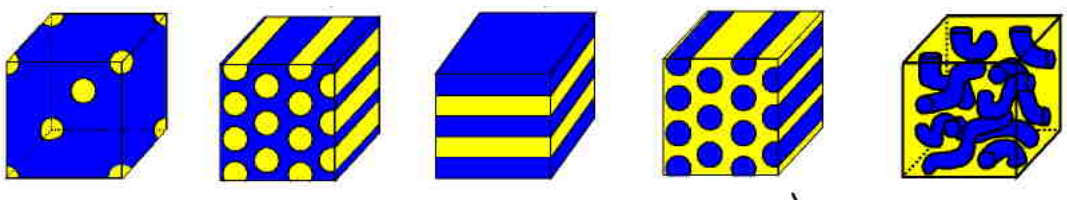
Nanostructured Materials via Self-assembly

Example: Diblock Copolymers



two inmiscible chains conncected by chemical bond



→ many morphologies (spheres, cylinders, lamellae)

→ typical microstructure periods of 10 nm to 100 nm

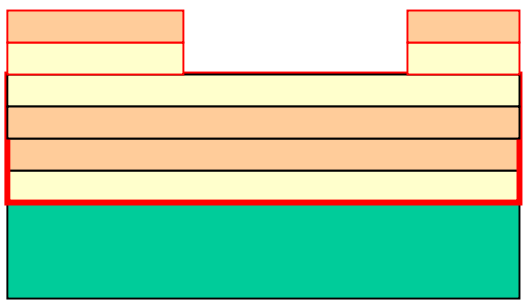
→ 3D powders with domain sizes of 1 μm to 10 μm

Block Copolymer Thin Films

interfaces air-polymer and polymer-substrate
give rise to preferential ordering

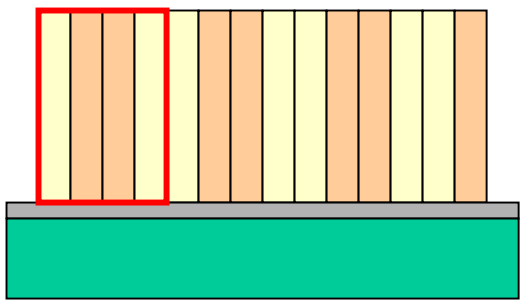
example: lamellar phase

strong preference:
of one block
to interface



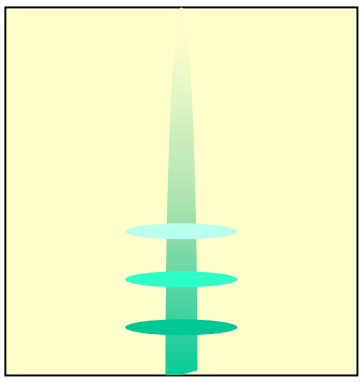
PS-PMMA /
Si oxide:
parallel lamellae

no preference:
chain-stretching
at interface

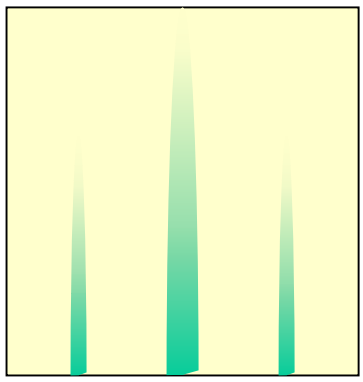


PS-PMMA /
PS-PMMA
random copolymer:
perpendicular lamellae

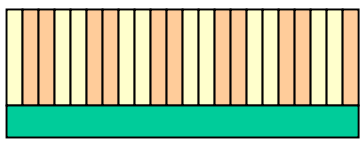
Scattering from a Lamellar System



CCD image



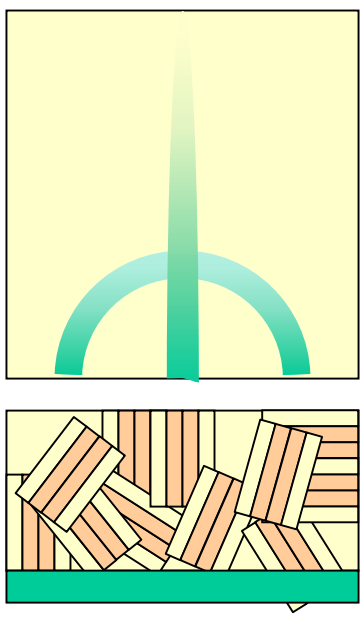
film



parallel

perpendicular

disordered or partially ordered



tilted

3D powder

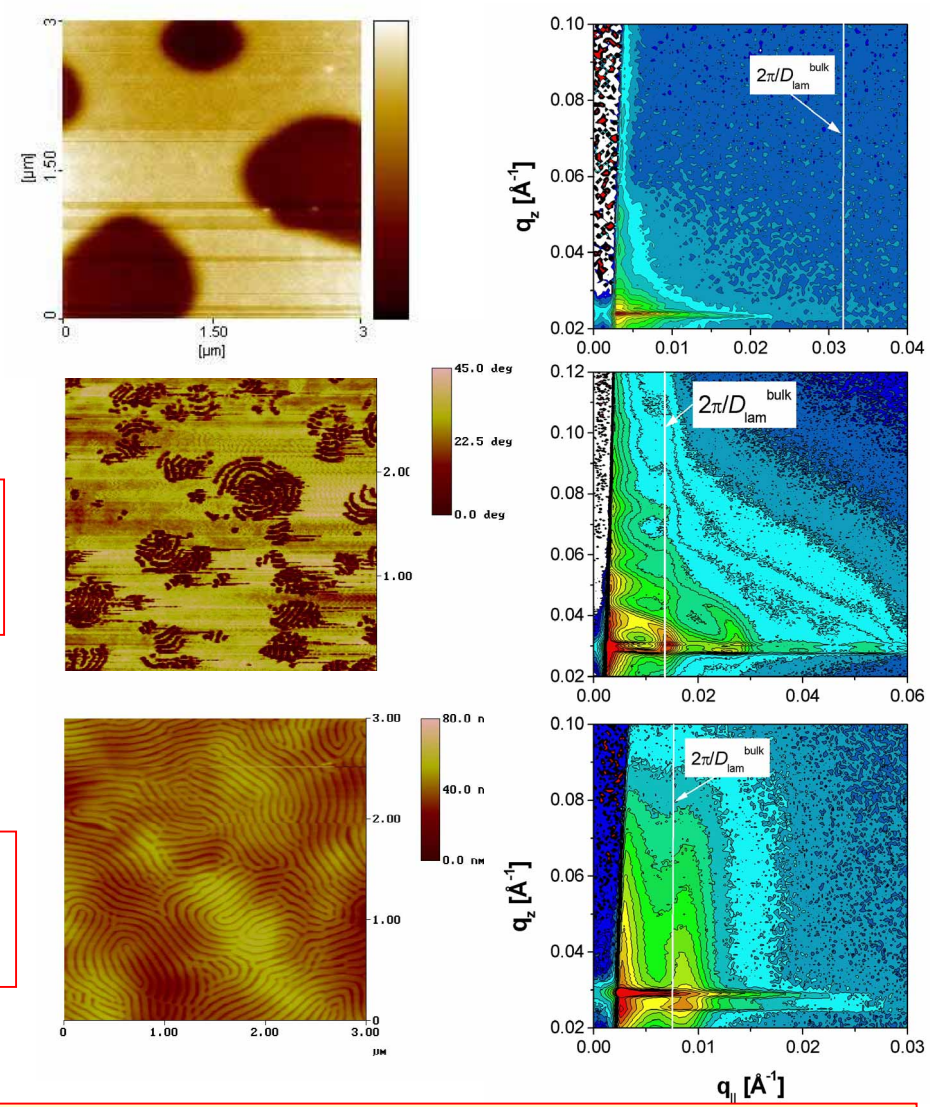
Polystyrene-Polybutadiene: A morphological transition

TM-AFM GISAXS

N= 300
Λ= 190 Å
D = 400 Å

N= 750
Λ= 410 Å
D = 1700 Å

N= 2500
Λ= 840 Å
D = 2300 Å



Chain-length dependent morphology:
Short chains (N < 400): parallel lamellae
Long chains (N > 1000): perp. lamellae

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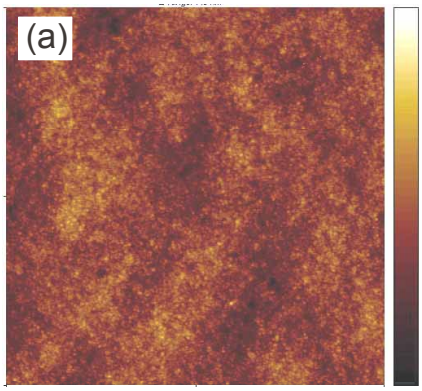
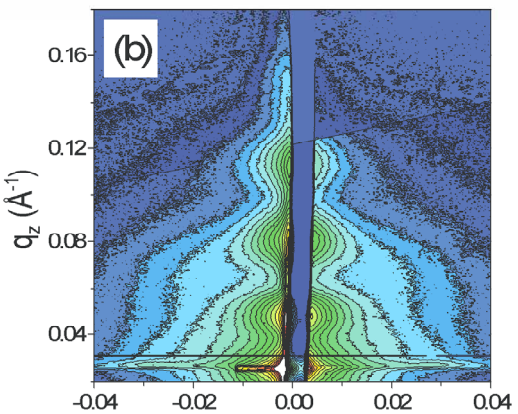
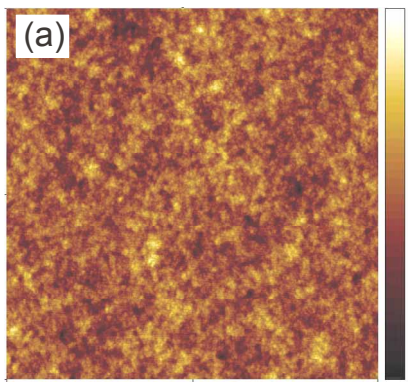
Copolymer Blends
or: What lies below the surface ?

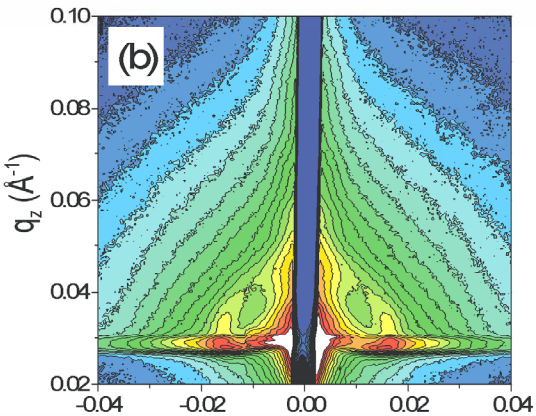
95% short chains



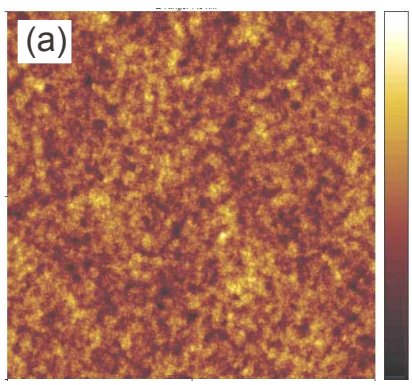


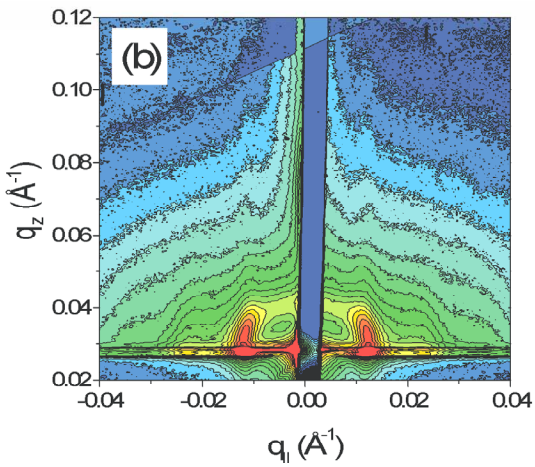
65%





40%





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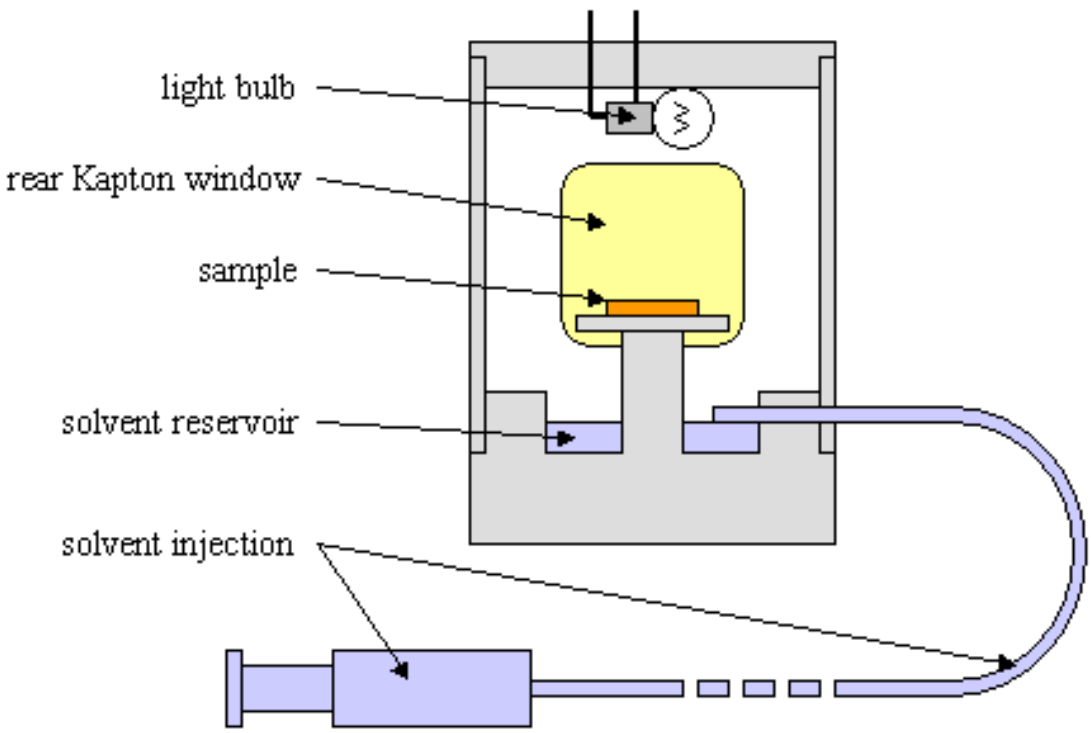
Time-Dependent Studies I: Stability of Polymer Films

Q: Are spin-coated polymer films stable?

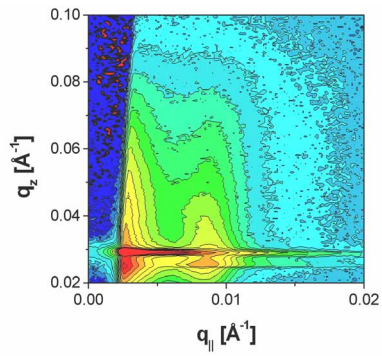
→ experiment: expose film to solvent vapor

sample cell

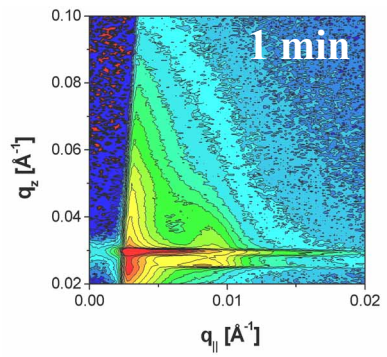


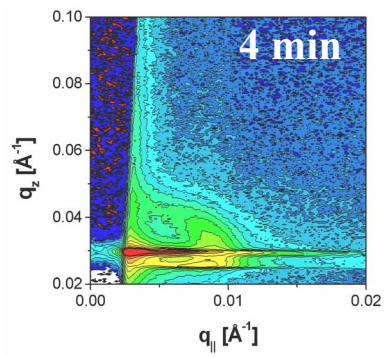
Time-Dependent Studies II: Swelling and Drying

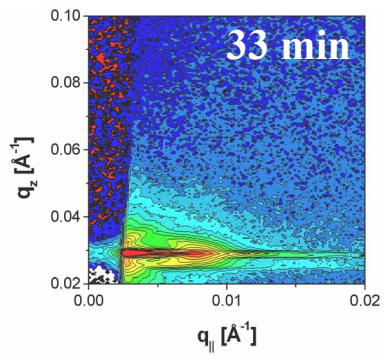
before vapor treatment



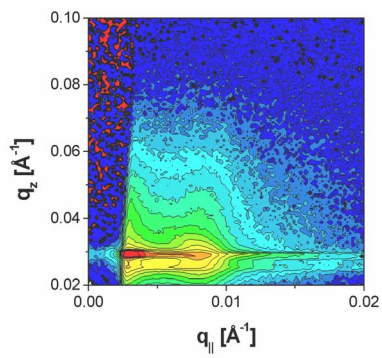
during exposure to toluene vapor







after drying for 10 min



Smilgies et al., SRN 15(5), 32 (2002).

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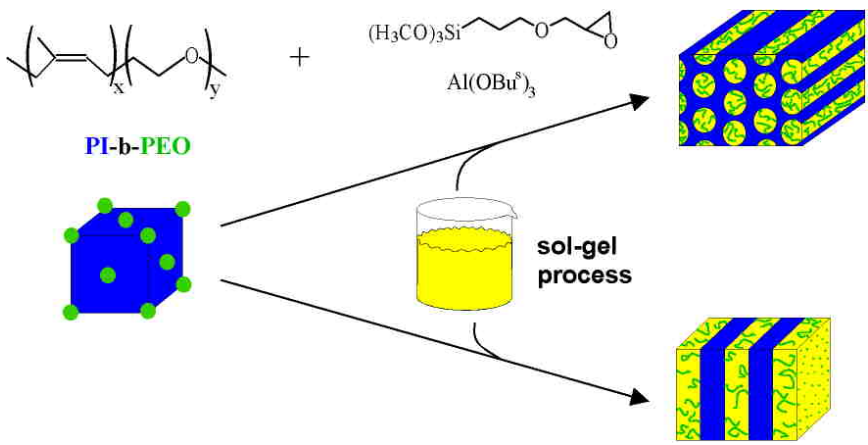
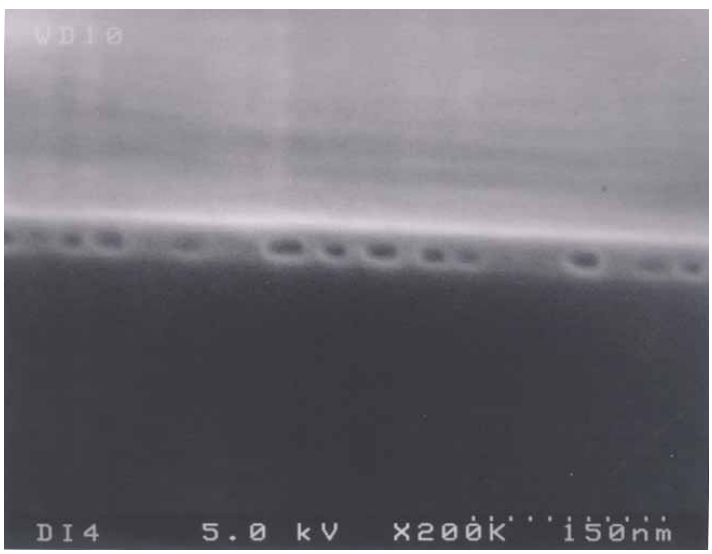
Nano-Composites



Example: matrix silicated, spheres organic

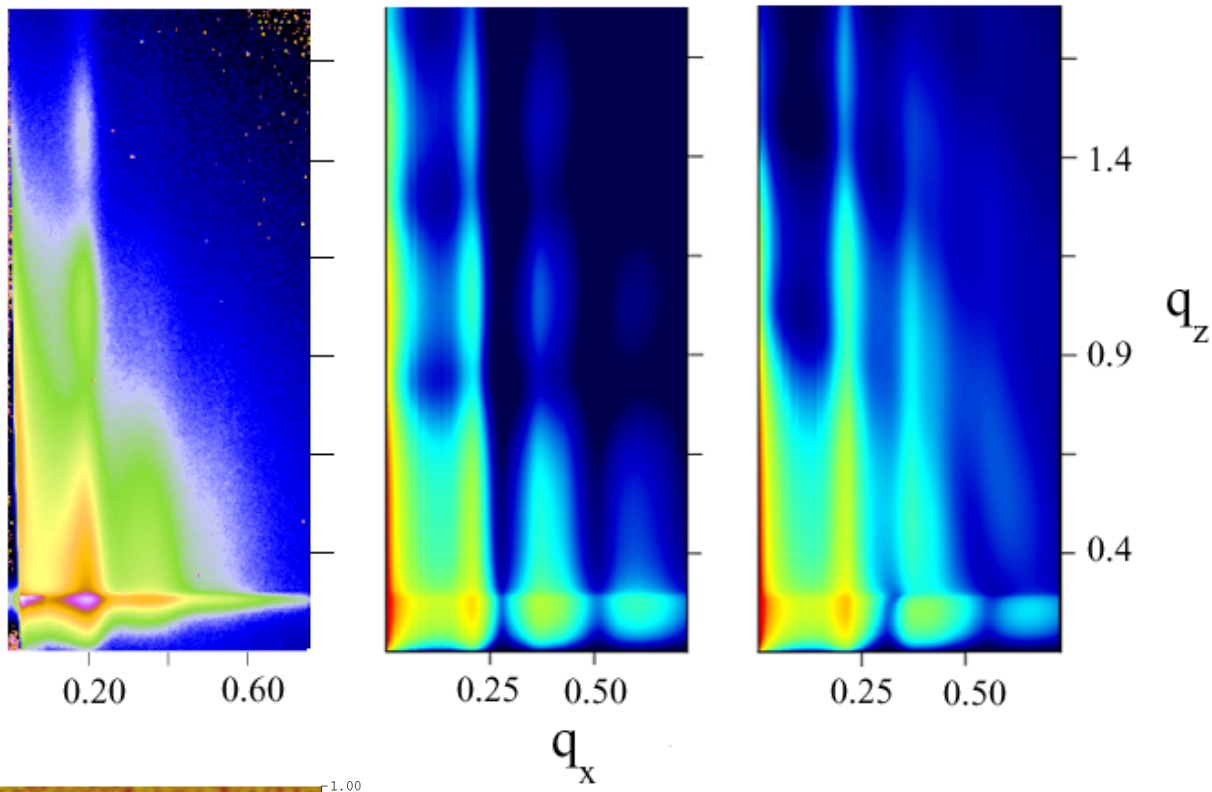


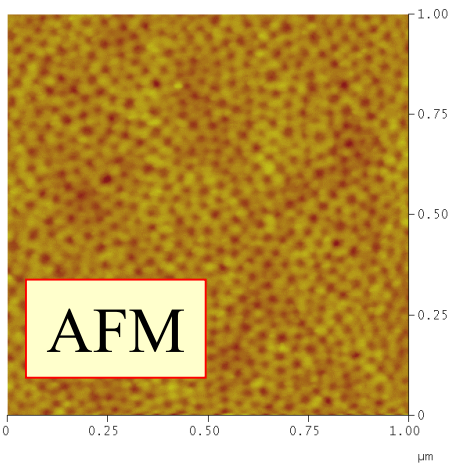
SEM edge on: monolayer of hollow spheres

GISAXS from a Monolayer of Voids

data

simulation





Du et al, Advanced Materials, accepted

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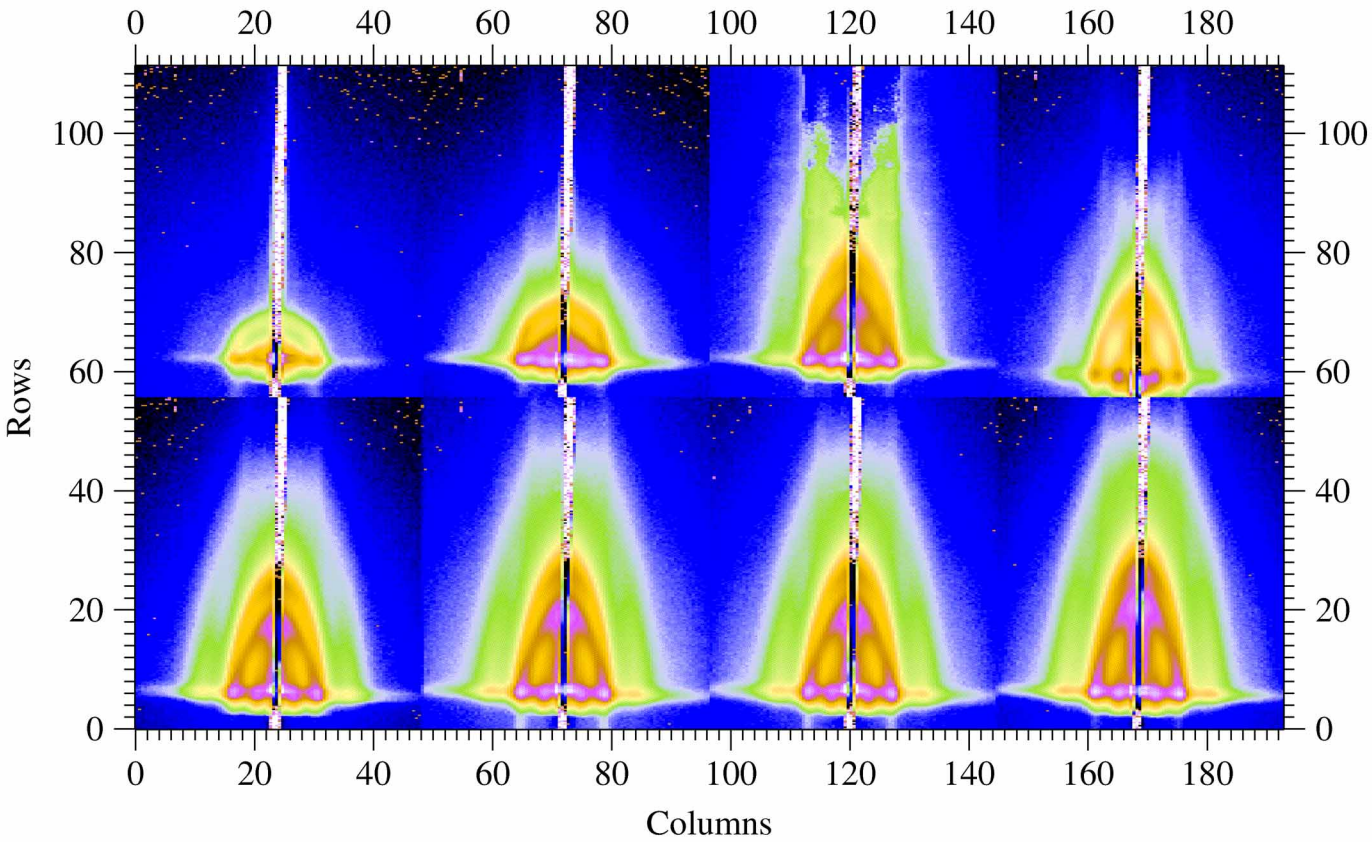
Time-Dependent Studies III: Calcination



Composit EO1
before, 100°C, 200 °C, 300 °C,
400 °C, 500 °C, after 10 min, back to RT

Summary: GISAXS

- **Mesoscopic length scales: 5-100 nm**
- **Surface sensitive**
- **Internal film structure**
- **In-situ experiments**
- **Real-time studies**

GISAXS - Availability

Cornell student Sterling Cornaby
aligning the new G1 GISAXS stage.

CHESS: D1 and G1
ESRF: ID1, ID10A&B, ID13
HASYLAB: BW2, BW4
LURE
NSLS : X22B

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